



## Dual-role plasticizer and dispersant for ceramic layers

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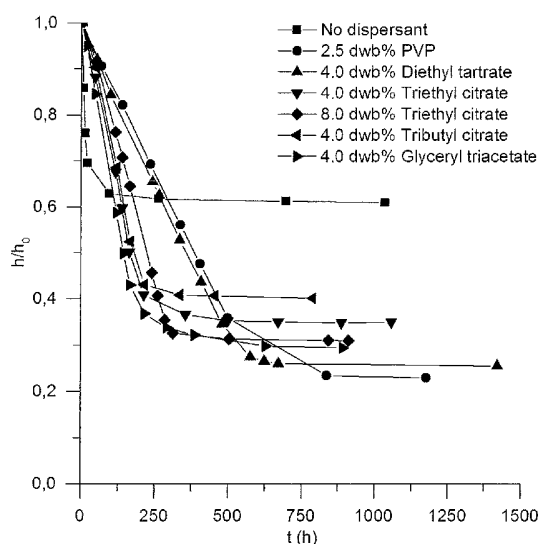
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## (54) Title: DUAL-ROLE PLASTICIZER AND DISPERSANT FOR CERAMIC LAYERS

Fig. 6



(57) Abstract: Thus, one aspect of the invention relates to a green ceramic layer comprising a ceramic material, a binder, and a dual-role dispersant and plasticizer, wherein said dual-role dispersant and plasticizer is an organic di- or tri-ester selected from compounds of formula (I), (II), (III) and (IV). Another aspect of the present invention relates to a slurry for use in the manufacturing of a green ceramic layer comprising a ceramic material, a solvent, a binder, and a dual-role dispersant and plasticizer, wherein said dual role dispersant and plasticizer is an organic di- or tri- ester. Further aspects include uses of and methods of manufacturing said green ceramic layers.



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## DUAL-ROLE PLASTICIZER AND DISPERSANT FOR CERAMIC LAYERS

### Technical field of the invention

The present invention relates to ceramic layers as used in for example solid oxide  
5 cell (SOC) technology and piezo-electronics. In particular the present invention  
relates to ceramic layers comprising an organic di- or tri- ester functioning in a  
dual-role as both plasticizer and dispersant.

### Background of the invention

- 10 Solid oxide cells (SOCs) generally include cells designed for different applications,  
such as solid oxide fuel cells (SOFCs) or solid oxide electrolysis cells (SOECs). Due  
to the common basic structure thereof, the same cell may be used in SOFC  
applications as well as in SOEC applications. Generally, SOC and also for example  
piezo-electronic components comprises one or more ceramic layers. Such ceramic  
15 layers must meet high standards during the stages of production (e.g. either in  
the slurry state, green state and/or sintered state) in relation to a number of  
factors including uniformity, reproducibility, durability, heat resistance, shape  
stability and viscoelasticity.
- 20 Ceramic layers may be manufactured using several different techniques which  
include for example tape-casting, screen printing, spraying and extrusion.  
Common for most of these techniques is that the components of the ceramic layer  
are dispersed in a solvent to form a slurry and applied using the selected method  
onto a support layer or surface. The slurry is subsequently dried to remove  
25 solvent and thus produce a green ceramic layer which may subsequently be  
sintered. Depending on the application the ceramic layer is subjected to "burnout"  
wherein organic materials are removed at elevated temperatures. Finally the  
ceramic layer is commonly sintered after solvent evaporation and burnout.  
Sintering is commonly performed at high temperatures in excess of 600 °C, as is  
30 the case e.g. within SOC technologies.

These methods presents a number of challenges in connection with meeting the  
demands for the ceramic layers mentioned above. Thus, to meet these demands

several additives are included in the slurry comprising the ceramic material and solvent, before forming the ceramic layer. These additives particularly include, but are not limited to, binders, plasticizers and dispersants.

Binders and plasticizer(s) are added to obtain a desired level of strength and flexibility of the resulting ceramic layer, e.g. before sintering, while dispersants are important additives in connection with obtaining a stable dispersion of the preliminary slurry and therefore a uniform density and microstructure of the final ceramic layer.

It is well-known that di- or tri-esters of for example citric acid or other carboxylic acids are suitable plasticizers for a range of polymers with various applications. Thus, WO 2013/022345 discloses the use of partly esterified sugar-based plasticizers for use with thermoplastic polymers mentioning esterified citrates, such as tributyl 2-acetylcitrate, as prior art. Likewise, US 2006/0198991 discloses the use of various citrate esters as plasticizers in functional layers of optical films (see e.g. [0078]). None of these documents disclose the simultaneous use of these esters as dispersants.

However, the addition of further chemicals to a ceramic layer presents problems due to e.g. undesirable chemical reactions, displacement of one component over another, entanglement effects, unexpected affinities, reactivity or shape deformation e.g. during sintering. These interactions may lead to undesirable interactions including agglomeration, flocculation, inhomogeneity, poor flow properties and uneven layer thickness and distorted layers.

Hence, a ceramic layer where fewer chemical additives are used would be advantageous, and in particular ceramic layers where one single chemical compound could act in more than one role, e.g. both as plasticizer and dispersant, would be advantageous.

Such dual-role chemical compounds have been reported for example in Prabhakaran et al., Journal of the European ceramic society, 21, 2001, 2873, where cardanol (a phenol substituted long-chain fatty acid) is used as both dispersant and plasticizer in alumina/toluene tape casting.

35

Organic di- and tri-esters have on the other hand not been reported as a dual-role plasticizer and dispersant.

Hidber et al. has discussed the use of non-esterified citric acid as a dispersant for aqueous alumina suspensions in Journal of the American Ceramic Society, 79, 1996, 1857-67. Hidber also discussed the influence of dispersant structure, for a number of non-esterified alcohols and carboxylic acids, for stabilization of aqueous alumina suspensions in, Journal of the European Ceramic Society, 17, 1997, 239-49. Nothing is disclosed regarding di- or tri- esters as dispersants and plasticiser.

EP 0361789 discloses certain mixed long chain esters of citric acid for use as pigment dispersants in paints. The esters applied therein do not have a dual-role and are not used in relation to ceramic layers and SOC's. The disclosed esters generally comprise alkyl chains of 10-carbon chain length or higher.

DE 1228736 discloses the use of distearyl citrate as a dispersant in paint compositions. The ester applied therein does not have a dual-role and is not used in relation to ceramic layers and SOC's. The disclosed stearyl ester comprises alkyl chains of 18-carbon chain length or higher.

EP 1552913 discloses the use of di- or tri-esters as a "dispersion medium" in the formation of *e.g.* green ceramics. However, the "dispersion medium" does not appear to act as "dispersant" since it is provided to react with the gelling agent to provide hardening of the ceramic. Nothing is disclosed about di- or tri-esters acting as effective small molecule dispersants or as dual role plasticizer and dispersants.

EP 1832337 discloses a method of coating *e.g.* ceramic powders with a "liquid dispersant" in the absence of a solvent, which includes the esters similar to the ones of the present invention. It is described how coating of the ceramic powder with liquid esters improves flowability of the powder. Nothing is disclosed about these esters for use in slowing down sedimentation in solvent solutions of ceramic materials comprising binders, or enhancing the plasticity and uniformity of ceramic materials comprising binders.

## Summary of the invention

Thus, an object of the present invention relates to providing alternative or improved ceramic layers comprising a dual-role compound providing for both viscoelasticity and uniformity in the resulting product. In other words the problem solved may be defined as the provision of an improved or alternative compound working as both a plasticizer and dispersant, e.g. in ceramic layers.

In particular, it is an object of the present invention to provide a green ceramic layer and methods for providing such layers that solves the above mentioned problems of the prior art with respect to providing green ceramic layers having good viscoelasticity and uniformity of density and microstructure while avoiding the problems related to the addition of a multitude of different chemicals ultimately resulting in cross-reactions, unexpected affinities which in turn leads to problems with e.g. uniformity in the resulting sintered ceramic layer.

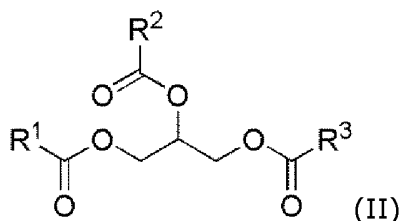
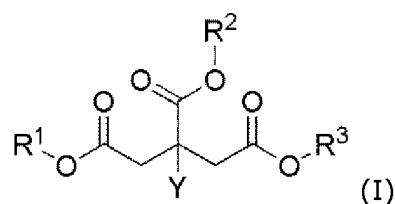
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Thus, one aspect of the invention relates to a green ceramic layer comprising

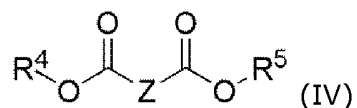
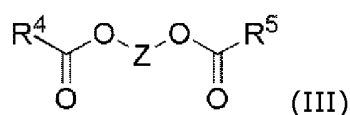
- a ceramic material,
- a binder, and
- a dual-role dispersant and plasticizer,

wherein said dual-role dispersant and plasticizer is an organic di- or tri-ester selected from a compound of formula (I), (II), (III) or (IV)

25



5



5

wherein

R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are independently selected from C<sub>1</sub>-C<sub>9</sub> alkyl and hydrogen, with the proviso that at least two of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> is a C<sub>1</sub>-C<sub>9</sub> alkyl,

Y is hydrogen or hydroxyl,

10 R<sup>4</sup> and R<sup>5</sup> are independently selected from C<sub>1</sub>-C<sub>9</sub> alkyl,

Z is C<sub>1</sub>-C<sub>6</sub> alkylene or C<sub>2</sub>-C<sub>6</sub> alkenylene wherein said alkylene or alkenylene is optionally substituted with hydroxyl.

Another aspect of the present invention relates to a slurry for use in the

15 manufacturing of a green ceramic layer comprising

- a ceramic material,
- a solvent
- a binder, and
- a dual-role dispersant and plasticizer,

20 wherein said dual role dispersant and plasticizer is an organic di- or tri-ester.

Yet another aspect of the present invention is the use of an organic di- or tri-ester as a dispersant in a slurry or green ceramic layer comprising a ceramic material.

25 Still a further aspect of the present invention is a method of manufacturing a green ceramic layer comprising the steps of

- a) mixing a dual role plasticizer and dispersant, a ceramic material and a solvent to provide a slurry
- b) milling the slurry provided in step a)
- 30 c) adding a binder to the milled slurry provided in step b)
- d) optionally homogenizing said slurry of step c)
- e) optionally de-airing and filtering said slurry of step c) or d)



f) shaping said slurry provided in either of step c) to e) optionally using a support substrate to form a layer

g) drying said slurry layer of step f) to provide said green ceramic layer, wherein said dual role dispersant and plasticizer is an organic di- or tri-ester.

5

The present inventors have surprisingly found that the use of organic di- and tri-esters as combined dispersant and plasticizers provide for improved green ceramic layers with fewer organic additives which in turn provides for simpler manufacturing processes and improved ceramic layers after burnout and sintering  
10 due to the reduction of interactions between organic materials during these final processing steps.

### **Brief description of the figures**

**Figure 1** shows specific qualitative features for specific combinations of PVB binder, a dual role plasticizer and dispersant (triethyl citrate) and a secondary  
15 plasticizer (PEG600). O means opaque, Sw means sweating, S means too strong, I means too inflexible, W means too weak, F means too flexible.  
"Primary/secondary candidates" exhibited an excellent combination of properties according to the definitions above.

20

**Figure 2** shows specific qualitative features for specific combinations of PVB binder, a dual role plasticizer and dispersant (tributyl citrate) and a secondary  
plasticizer (PEG600). O means opaque, Sw means sweating, S means too strong, I means too inflexible, W means too weak, F means too flexible.  
25 "Primary/secondary candidates" exhibited an excellent combination of properties according to the definitions above.

**Figure 3** shows specific qualitative features for specific combinations of PVB binder, dual role plasticizer and dispersant (dibutyl maleate) and a secondary  
30 plasticizer (PEG600). O means opaque, Sw means sweating, S means too strong, I means too inflexible, W means too weak, F means too flexible.  
"Primary/secondary candidates" exhibited an excellent combination of properties according to the definitions above.

**Figure 4** shows specific qualitative features for specific combinations of PVB binder, a dual role plasticizer and dispersant (triethyl 2-acetylcitrate) and a secondary plasticizer (PEG600). O means opaque, Sw means sweating, S means too strong, I means too inflexible, W means too weak, F means too flexible.

- 5 "Primary/secondary candidates" exhibited an excellent combination of properties according to the definitions above.

**Figure 5** shows specific qualitative features for specific combinations of PVB binder, a dual role plasticizer and dispersant (tributyl 2-acetylcitrate) and a  
10 secondary plasticizer (PEG600). O means opaque, Sw means sweating, S means too strong, I means too inflexible, W means too weak, F means too flexible.

"Primary/secondary candidates" exhibited an excellent combination of properties according to the definitions above.

- 15 **Figure 6** shows sedimentation profiles for a dispersion comprising 3YSZ in ethanol without a dispersant (reference) and for dispersions comprising 3YSZ and 2.5 dwb% PVP (reference), 4 dwb% diethyl tartrate, 4 dwb% triethyl citrate, 8 dwb% triethyl citrate, 4 dwb% tributyl citrate or 4 dwb% glyceryl triacetate in ethanol (dwb meaning 'dry weight basis').

20

**Figure 7** shows a SEM picture of a sintered ceramic layer as produced by the tape casting method described in example 1 employing a dual role plasticizer and dispersant in the form of tributyl citrate.

- 25 **Figure 8** shows a picture of a uniform green ceramic layer produced by the tape casting method of example 1.

**Figure 9** shows a picture of a uniform sintered ceramic layer produced by the tape casting method of example 1.

30

The present invention will now be described in more detail in the following.

## Detailed description of the invention

### Definitions

Prior to discussing the present invention in further details, the following terms and conventions will first be defined:

5

In the present context "*ceramic layer*" means a material capable of serving as a layer comprising a ceramic material. Often a ceramic layer will be in a sheet type structure. The thickness may vary from sub-micrometer to several centimeters. In the present context a ceramic layer is typically durable and viscoelastic, whereas  
10 it becomes significantly less viscoelastic upon sintering, either as a monolayer or as part of a multi-layer structure.

In the present context "*ceramic material*" means an inorganic material compounded of at least one metal and of at least one non-metal. They may be  
15 crystalline or amorphous and can often withstand very high temperatures without degrading. Ceramic materials may be ionic-conducting, electronic-conducting, mixed ionic and electronic conducting, semi-conducting or insulators. Ceramic materials may be doped with small amounts of other substances (i.e. dopants, such as metals) to adapt their properties. Examples of ceramic materials include  
20 metal oxides such as zinc oxide and also substances like alumina, and ceria.

In the present context "*binder*" means any material capable of functioning as a binding material in ceramic layers to produce a durable and flexible layer, preferably polymeric binders. In the present context such binders are typically  
25 carbon-based and thermo-stable polymers, i.e. polymers that are stable at temperatures up to several hundred degrees Celsius. Examples include polyvinyl and polyethylene type polymers. Binders that are synthesised in-situ by cross-linking using e.g. gelling agents and catalysts, such as during gel-casting, are not included.

30

In the present context "*dual-role dispersant and plasticizer*" means any compound that may function as both a plasticizer and dispersant in the context of e.g. ceramic layers. Further "*dispersant*" means any substance capable of maintaining a stable dispersion longer than the corresponding dispersion without dispersant,  
35 i.e. any substance that slows down particles agglomeration and consequently

prolongs the process of settling or sedimentation of particles in liquid dispersion/slurry and during drying of such a dispersion or slurry. A dispersant will generally help particle wetting in the milling stage and prevents re-agglomeration during and after milling is concluded. Finally, "*plasticizer*" may in the broadest  
5 sense mean any substance capable of increasing the flexibility of a solid material comprising a binder.

In the present context "*organic di- or tri-ester*" means an organic compound comprising at least two groups of the general formula  $RC(O)O-CR'_3$ . In this  
10 context R and R' may be any moiety including further optionally substituted alkyls, hydrogens, halogens, and heteroatoms including O, S, N and P.

In the present context "*alkyl*" means any optionally substituted terminal hydrocarbon chain, including branched or linear chains. Examples include methyl ( $-CH_3$ ), ethyl ( $-CH_2CH_3$ ), propyl ( $-CH_2CH_2CH_3$ ) and isobutyl ( $-CH(CH_3)CH_2CH_3$ ).  
15 "*alkylene*" means any non-terminal optionally substituted hydrocarbon chain, including branched or linear chains. Examples include methylene ( $-CH_2-$ ) and 2-methyl-propylene ( $-CH_2-CH(CH_3)-CH_2-$ ) while "*alkenylene*" means any non-terminal optionally substituted hydrocarbon chain comprising at least one double bond, including branched or linear chains. Examples include ethylene ( $-CH=CH-$ )  
20 and 1-butylene ( $-CH=CH-CH_2-CH_2-$ ).

In the present context "slurry" means a mixture of a liquid and solid particles that retain some fluidity.

25 In the present context "viscosity" means the viscosity of a slurry and is defined relative to the viscosity of the liquid phase. The viscosity depends among others on the size and concentration of the particles contained within the slurry. Viscosity decreases with decreasing size and concentrations of the particles. Furthermore, the viscosity decreases with increasing temperature of the slurry. The viscosity is  
30 not to be confused with viscoelasticity which is a property of the green ceramic layer describing both the viscous and elastic characteristic of a material undergoing deformation.

In the present context "flow" means the motion of a fluid only affected by gravity.  
35 An example of a fluid that flows under the influence of gravity is a slurry, whereas

a thicker paste without any solvent present may instead flow under applied pressure, e.g. by extrusion.

In the present context "milling" refers to the use of a ball mill for grinding and  
5 blending of materials. During milling the size of particles within a composition, such as a slurry, is reduced upon impact of the balls within the ball mill. The balls may be beads made from alloys such as stainless steels or ceramics such as alumina or zirconia. Milling may also be used for homogenization of solutions containing solid particles.

10

The first aspect of the present invention is a green ceramic layer comprising

- a ceramic material,
- a binder, and
- a dual-role dispersant and plasticizer,

15 wherein said dual-role dispersant and plasticizer is an organic di- or tri-ester.

An alternative to the first aspect of the present invention is a green ceramic layer comprising

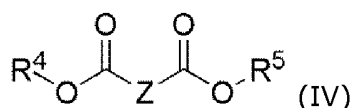
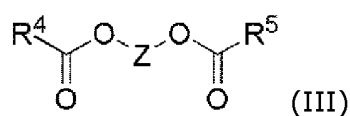
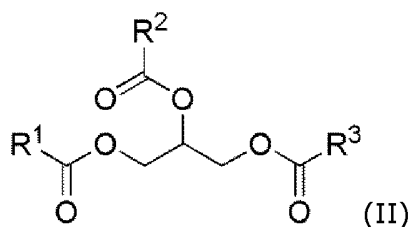
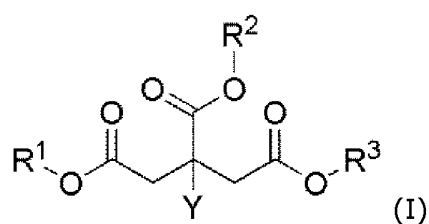
- a ceramic material,
- 20 - a binder, and
- an organic di- or tri-ester.

In a preferred embodiment the green ceramic layer as defined above comprises no further dispersants, i.e. the combined plasticizer and dispersant provides  
25 sufficient dispersion in addition to its plasticizing effect to negate the need for any further dispersants. Although additional plasticizers may be added, in another embodiment the green ceramic layer comprises no further plasticizers. Preferably the organic di- or tri-ester is a carboxylic acid ester. Particularly, organic di- or tri-ester does preferably not include phosphate esters.

30

The organic di- or tri-ester may preferably be selected from a compound of formula (I), (II), (III) or (IV)

11



5

10 wherein

$R^1$ ,  $R^2$  and  $R^3$  are independently selected from  $C_1$ - $C_9$  alkyl and hydrogen, with the proviso that at least two of  $R^1$ ,  $R^2$  and  $R^3$  is a  $C_1$ - $C_9$  alkyl,

$Y$  is hydrogen or hydroxyl,

$R^4$  and  $R^5$  are independently selected from  $C_1$ - $C_9$  alkyl,

15  $Z$  is  $C_1$ - $C_6$  alkylene or  $C_2$ - $C_6$  alkenylene wherein said alkylene or alkenylene is optionally substituted with hydroxyl.

Preferably said alkylene or alkenylene is substituted with one or more hydroxyl groups. This group of compounds shares the features of having at least two ester  
20 groups and also at least two small to medium size alkyl group. As described above known plasticizers fall within this group of compounds, but they have not been reported to have dispersion capabilities let alone combined plasticizer and dispersion abilities.

In a preferred embodiment the alkylene or alkenylene can have some of the hydrogen atoms substituted with hydroxyl functional groups.

In a preferred embodiment  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are independently selected from  
5 C<sub>1</sub>-C<sub>6</sub> alkyl.

A preferred organic di- or tri ester is a compound as defined above wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are independently selected from C<sub>1</sub>-C<sub>6</sub> alkyl

Y is hydroxyl

Z is C<sub>1</sub>-C<sub>6</sub> alkylene wherein said alkylene is optionally substituted with hydroxyl.

10

Preferably Z may be a group of the formula  $-(CH_2)_m(CH[OH])_p(CH_2)_n-$ , where m and n and p independently are selected from an integer between 0 and 6, preferably with the proviso that  $m+p+n$  is between 1 and 6. Most preferably Z is selected from the group consisting of  $-CH_2CH[OH]CH_2-$ ,  $CH_2CH[OH]-$  and

15  $-CH[OH]CH[OH]-$ .

The organic esters of the present invention may also be defined in terms of the carboxylic acid or polyol on which they are based. Thus another preferred embodiment of the present invention is a green ceramic layer as defined above,  
20 wherein said organic di- or tri-ester is a di- or tri-ester of a carboxylic acid or a polyol selected from the group consisting of citric acid, oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid, glutaric acid, adipic acid, malic acid, tartaric acid, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexamethylene glycol and glycerol. A particularly preferred group of esters are an  
25 organic di- or tri-ester of a carboxylic acid or a polyol selected from the group consisting of citric acid, malic acid, tartaric acid and glycerol.

The present inventors have surprisingly found that the ester of the invention should preferably comprise carbon chains of small to medium size. This is  
30 particularly the case for the alkyl groups bound directly to either the carboxyl or oxygen of the ester moiety. Thus the best combined plasticization and dispersion effect is obtained when the longest alkyl chains are between 1 and 9 carbons in length. Thus, in a preferred embodiment said organic di- or tri-ester comprises no alkyl chains comprising more than 9 carbons, such as preferably no alkyl chains  
35 comprising more than 8 carbons, 7 carbons, 6 carbons, 5 carbons, most

preferably no alkyl chains comprising more than 4 carbons. A preferred chain length of the comprised alkyl groups is 2-6 carbons, such as preferably 2-4 carbons. Further, the inventors have found that a di- or tri- ester comprising at least one free hydroxyl group improves the dual plasticizer/dispersant effect of  
5 said ester. Thus, in a preferred embodiment the organic di- or tri- ester comprises at least one free hydroxyl group.

In yet another embodiment said organic di- or tri-ester is selected from the group consisting of triethyl citrate, tributyl citrate, glyceryl triacetate and diethyl  
10 tartrate.

The amount of dual-role plasticizer and dispersant depends on the other components of the green ceramic layer and the process and solvents used for making the ceramic layer. However, in a preferred embodiment of the green  
15 ceramic layer of the present invention said dual role dispersant and plasticizer is present in amount on dry weight basis (dwb) of 0.1-30%(dwb), 0.2-25%(dwb), 0.5-20%(dwb), 1-18%(dwb), 2-17%(dwb), 3-16%(dwb), 5-15%(dwb), 8-12%(dwb), 9-11%(dwb), such as around 10%(dwb).

20 The ceramic material is in the present invention preferably a powder. Generally, the particle size of the ceramic material is adjusted so as to allow proper dispersion in the selected solvent and thus provide a suitable slurry for the formation of a green ceramic layer upon drying said slurry after processing into a layer form. Preferably, the average particle diameter (median) of the ceramic  
25 material in the ceramic layer is less than 1.0  $\mu\text{m}$ , such as less than 0.8  $\mu\text{m}$ , less than 0.6  $\mu\text{m}$ , less than 0.4  $\mu\text{m}$ , less than 0.3  $\mu\text{m}$ , preferably less than 0.2  $\mu\text{m}$ . Preferably the ceramic material is a metal oxide or mixed oxide. In a preferred embodiment the ceramic material is selected from the group consisting of cerias, zirconas, perovskites, spinels, aluminas, titanias, and any mixtures thereof. Said  
30 ceramic material may preferably be doped with an additional substance. Said substance may preferably be a material selected from the group consisting of gadolinium, yttria, praseodymium, scandia, and any mixtures thereof. Preferably Gd and Pr would only be added in relation with ceria and Y and Sc only with zirconia.



The binder of the present invention is important for the formation of a coherent green ceramic layer, which is durable upon handling. In a preferred embodiment said binder is a polymeric binder. Polymeric binders may be selected from the group consisting of poly(vinyl butyral) (PVB), cellulose ethers including methyl  
5 and ethyl cellulose, poly(vinyl alcohol) (PVA), poly(ethylene glycol) (PEG), poly(vinyl pyrrolidone) (PVP), poly(vinyl acetate), poly(vinyl methyl methacrylate) and any mixtures thereof. A particularly preferred binder is poly(vinyl butyral) (PVB). Preferably the binder has a molecular weight between 10-200 kDa, such as 20-175 kDa, such as 30-150 kDa, such as 40-100 kDa, preferably 50-75 kDa.

10

The green ceramic layer may comprise further additives, including for example additional plasticizer. Even though the compounds of the present invention are well-known for having plasticizing effects, this effect may be supplemented further by secondary plasticizers. Thus in an advantageous embodiment said ceramic  
15 layer comprises at least one secondary plasticizer. Said secondary plasticizer may preferably be poly(ethylene glycol) (PEG) or poly(propylene glycol) (PPG). PEG200-PEG1000 or PPG200-PPG1000 are preferred secondary plasticizers. Examples of particularly suitable PEG's and PPG's are selected from the group consisting of PEG400, PEG600, PPG400 and PPG600.

20

Further additives may also be comprised in the green ceramic layer, thus said green ceramic layer may comprise additives such as additives selected from the group consisting of a releasing agent, a de-foaming agent, fungicides, pesticides and/or a flow modifier. There are a number of techniques available for providing  
25 green ceramic layers, which are all well-known to the skilled person in the art. Thus a green ceramic layer may be produced using a technique selected from but not limited to the group consisting of tape-casting, screen printing, extrusion, slip-casting, slot die coating and spraying. Common for all these techniques is that the mixture of ceramic material, binder and dispersant/plasticizer and any further  
30 additives are provided as a slurry in a suitable solvent. The green ceramic layer is initially shaped from said slurry, typically on a supporting layer or sheet followed by drying to form a more solid green ceramic layer. These layers may then proceed to be cut into suitable sizes and either become part of multi-layered structures such as e.g. solid oxide cells, and be subject to e.g. sintering either

before or after multi-layer assembly. A particularly preferred technique is tape-casting.

Preferred techniques for providing green ceramic layers are tape-casting, screen  
5 printing, slip-casting, slot die coating and spraying. Common for all these techniques is that the mixture of ceramic material, binder and dispersant/plasticizer and any further additives are provided as a slurry in a suitable solvent.

10 In an embodiment of the present invention it is preferred to provide green ceramic layers that are thin, such as 100 nm to 10 cm, such as 0.5  $\mu\text{m}$  to 1 cm preferably 1  $\mu\text{m}$  – 1 mm.

For production of thin ceramic layers it is advantageous to use a solution of  
15 ceramic materials with low viscosity because it is difficult to obtain thin layers that are sufficiently homogeneous without any agglomeration and of even thickness from high viscosity fluids. Consequently, it is preferred to work with ceramic materials in the presence of a solvent, *i.e.* as a slurry, in contrast to ceramic materials in the absence of a solvent, *i.e.* as a paste.

20

In one embodiment of the present invention, the slurry containing the ceramic materials has a low viscosity, such as 1 mPa · s to 100 Pa · s, preferably 10 mPa · s to 10 Pa · s.

25 A preferred method for providing a thin ceramic layer may be, but not limited to, tape-casting or other techniques suitable for handling low viscosity slurries. In contrast a common technique for providing ceramic layers from a paste would be by extrusion.

30 The green ceramic layer may thus be a solid green ceramic layer. It may further be a dried green ceramic layer. The green ceramic layer may preferably be sintered to produce a final ceramic layer. Particularly, the ceramic layer may be sintered having been subjected to at least 600 °C, such as at least 650 °C, at least 700 °C, such as preferably at least 800 °C. A preferred temperature range  
35 for sintering is 600-2500 °C, such as 600-1500 °C.

The present invention allows for a more stable and homogenous distribution of the ceramics. It also allows a possible reduction in the organic content, due to the re-use of one component in more than one role. The reduction in organic content in turn allows for less shrinkage during sintering as well as a lower sintering  
5 temperature and/or duration due to the closer initial proximity of the ceramic powders.

In one advantageous embodiment said ceramic layer is for use within solid oxide cell (SOC) technology. Solid oxide fuel cells (SOFCs) are well known in the art and  
10 are available in various designs. Typical configurations include an electrolyte layer sandwiched in between two electrodes, i.e. an anode (fuel electrode) and a cathode (air electrode). The function of an anode in the SOFC is to react electrochemically with the fuel, which may be hydrogen and hydrocarbons, while the cathode reacts with oxygen to produce electric current. The electrodes are  
15 usually porous oxide layers of electronic or mixed ionic/electronic materials and/or composites. The electrolyte is typically a dense oxide ionic conductive material. Between the electrolyte and an electrode, e.g. the cathode, a dense barrier layer may be inserted to prevent chemical interaction between the cathode and the electrolyte materials. A further aspect of the present invention is a solid oxide cell  
20 comprising a sintered ceramic layer as defined herein.

In an alternative embodiment said ceramic layer is for use within piezo-electronic technology. Certain ceramic materials exhibit piezoelectric properties, and may be used within this field. Thus, a further aspect of the present invention is a piezo-electronic device comprising a ceramic layer according to the present invention.  
25

Another aspect of the present invention is a slurry for use in the manufacturing of a green ceramic layer comprising

- a ceramic material,
- a solvent
- 30 - a binder, and
- a dual-role dispersant and plasticizer,

wherein said dual role dispersant and plasticizer is an organic di- or tri-ester.

The slurry corresponds to the green ceramic layer of the present invention with  
35 the additional presence of a suitable amount of solvent. The slurry is preferably a

dispersion. Upon drying the green ceramic layer is essentially free of solvent, i.e. the remaining solvent in the green ceramic layer is less than 5% (w/w), such as less than 4%, 3%, 2%, 1%, 0.1%, 0.001% (w/w). Preferably said solvent is a polar organic solvent. Suitable solvents include methanol, ethanol, propanol, isopropanol, 1-butanol, 2-butanol, acetone as well as 2-butanone. Particularly preferred solvents are ethanol, propanol and isopropanol. The preferred embodiments of the green ceramic layer aspect of the present invention also apply to the present slurry aspect when applicable.

Thus, in a preferred embodiment of the slurry of the present invention said dual role dispersant and plasticizer is present in amount on dry weight basis (dwb) of 0.1-30%(dwb), 0.2-25%(dwb), 0.5-20%(dwb), 1-18%(dwb), 2-17%(dwb), 3-16%(dwb), 5-15%(dwb), 8-12%(dwb), 9-11%(dwb), such as around 10%(dwb).

Another aspect of the present invention is the use of an organic di- or tri-ester as a dispersant in the manufacture of a slurry or green ceramic layer comprising a ceramic material. In a preferred embodiment of said use, the green ceramic layer further comprises a binder. The ceramic layer may be for use within solid oxide cell (SOC) technology or the ceramic layer may be for use within piezoelectronic technology. The preferred embodiments of the ceramic layer aspect of the present invention also apply to the present use aspect when applicable.

Yet a further aspect of the present invention is a method of manufacturing a green ceramic layer comprising the steps of

- a) mixing a dual role plasticizer and dispersant, a ceramic material and a solvent to provide a slurry
- b) milling the slurry provided in step a)
- c) adding a binder to the milled slurry provided in step b)
- d) optionally homogenizing said slurry of step c)
- e) optionally de-airing and filtering said slurry of step c) or d)
- f) shaping said slurry provided in either of step c) to e) optionally using a support substrate to form a layer
- g) drying said slurry layer of step f) to provide said green ceramic layer, wherein said dual role dispersant and plasticizer is an organic di- or tri-ester.

In a preferred embodiment of the present invention, said manufacturing of a green ceramic layer is performed at a temperature of 0-50 °C, preferably at 5-40 °C, more preferably at 10-35 °C, even more preferably at 15-30 °C.

- 5 Preferably said solvent is a polar organic solvent. Homogenization is performed by using ball milling. Filtering is performed by pressing the slurry through a fine mesh filter with openings in the range from 10-200 micron depending on e.g. the final shaping technique and layer thickness needed. By de-airing is meant the removal of un-wanted air/gas in the slurry. This may be provided in a number of  
10 ways including evacuation, ultra-sonication or simply slow rolling for an extended period of time (hours to days), all of which are well known to the skilled person.

In a preferred embodiment said method further comprises the steps of

- h) optionally laminating said ceramic layer with further ceramic layers to  
15 form a multi-layered structure,

i) optionally performing a burnout of said ceramic layer

j) sintering said ceramic layer(s),

to provide a sintered ceramic layer. With step j) included, this embodiment is a method for the manufacture of a sintered ceramic layer.

20

In the above methods the cited order of performing steps a)-j) is preferred, but it is to be understood that some steps may be interchanged. Cooling of the sintered ceramic layer(s) is a further optional step (step k)).

- 25 A burnout is performed by slow heating to remove organic materials in a controlled fashion. It is performed at temperatures up to 600 °C.

- In one embodiment said sintering is performed at a temperature of 600-2500 °C, such as 600-1500 °C. In another embodiment said sintering temperature is above  
30 600 °C. This is normally performed in multiple steps with slow heating to start with to allow for the removal of the organic components followed by a dwell step at the desired sintering temperature to ensure e.g. proper densification, formation of the right ceramic phases, reaction between ceramic components etc. The cooling can either be fast to trap phases which are only stable at high

temperatures or slow to prevent a thermal shock which can create defects such as cracks in the sintered piece.

It should be noted that embodiments and features described in the context of one of the aspects of the present invention also apply to the other aspects of the invention.

Below are described items of the present invention of particular interest.

10 Item 1. A green ceramic layer comprising

- a ceramic material,
- a binder, and
- a dual-role dispersant and plasticizer,

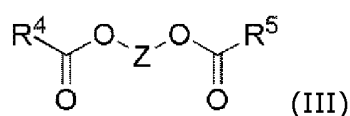
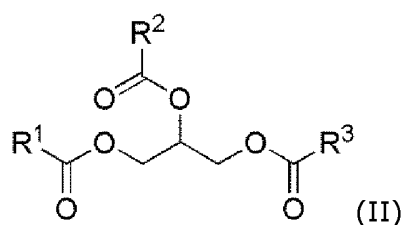
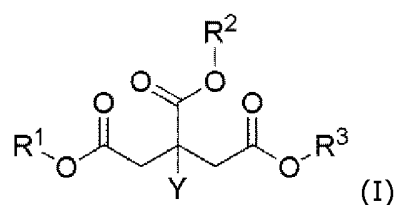
wherein said dual-role dispersant and plasticizer is an organic di- or tri-ester.

15

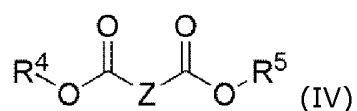
Item 2. A ceramic layer according to item 1, wherein said ceramic layer comprises no further dispersants.

Item 3. A ceramic layer according to any one of items 1-2, wherein said organic di- or tri-ester is selected from a compound of formula (I), (II), (III) or (IV)

25



20



wherein

- 5  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are independently selected from  $\text{C}_1$ - $\text{C}_9$  alkyl and hydrogen, with the proviso that at least two of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  is a  $\text{C}_1$ - $\text{C}_9$  alkyl,  
 $\text{Y}$  is hydrogen or hydroxyl,  
 $\text{R}^4$  and  $\text{R}^5$  are independently selected from  $\text{C}_1$ - $\text{C}_9$  alkyl,  
 $\text{Z}$  is  $\text{C}_1$ - $\text{C}_6$  alkylene or  $\text{C}_2$ - $\text{C}_6$  alkenylene wherein said alkylene or alkenylene is  
 10 optionally substituted with hydroxyl.

Item 4. A ceramic layer according to item 3, wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$  are independently selected from  $\text{C}_1$ - $\text{C}_6$  alkyl and hydrogen, with the proviso that at least two of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  is a  $\text{C}_1$ - $\text{C}_6$  alkyl.

15

Item 5. A ceramic layer according to any one of items 3-4, wherein  
 $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$  are independently selected from  $\text{C}_1$ - $\text{C}_6$  alkyl  
 $\text{Y}$  is hydroxyl  
 $\text{Z}$  is  $\text{C}_1$ - $\text{C}_6$  alkylene wherein said alkylene is optionally substituted with hydroxyl.

20

Item 6. A ceramic layer according to any one of items 3-5, wherein  $\text{Z}$  is –  
 $(\text{CH}_2)_m(\text{CH}[\text{OH}])_p(\text{CH}_2)_n$ -, and wherein  $m$ ,  $p$  and  $n$  independently are an integer  
 between 0 and 6, with the proviso that  $m+p+n$  is an integer between 1 and 6.

- 25 Item 7. A ceramic layer according to any one of items 3-6, wherein  $\text{Z}$  is selected from the group consisting of  $-\text{CH}_2\text{CH}[\text{OH}]\text{CH}_2-$ ,  $\text{CH}_2\text{CH}[\text{OH}]$ -, and  $-\text{CH}[\text{OH}]\text{CH}[\text{OH}]$ -.

- Item 8. A ceramic layer according to any one of the preceding items, wherein said  
 30 organic di- or tri-ester is a di- or tri-ester of a carboxylic acid or a polyol selected from the group consisting of citric acid, oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid, glutaric acid, adipic acid, malic acid, tartaric acid, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexamethylene glycol and glycerol.

Item 9. A ceramic layer according to item 8, wherein said organic di- or tri-ester is a di- or tri-ester of a carboxylic acid or a polyol selected from the group consisting of citric acid, malic acid, tartaric acid and glycerol.

- 5 Item 10. A ceramic layer according to any one of the preceding items, wherein said organic di- or tri-ester is selected from the group consisting of triethyl citrate, tributyl citrate, glyceryl triacetate and diethyl tartrate.

- Item 11. A ceramic layer according to any one of the preceding items, wherein  
10 said organic di- or tri-ester comprises no alkyl chains comprising more than 9 carbons, such as preferably 8 carbons, 7 carbons, 6 carbons, 5 carbons, most preferably 4 carbons.

- Item 12. A ceramic layer according to any one of the preceding items, wherein  
15 said dual role dispersant and plasticizer is present in amount of 0.1-30%(dwb), 0.2-25%(dwb), 0.5-20%(dwb), 1-18%(dwb), 2-17%(dwb), 3-16%(dwb), 5-15%(dwb), 8-12%(dwb), 9-11%(dwb), such as around 10%(dwb).

- Item 13. A ceramic layer according to any one of the preceding items, wherein  
20 said ceramic material is a powder.

- Item 14. A ceramic layer according to any one of the preceding items, wherein said ceramic material is a metal oxide or mixed oxide, preferably selected from the group consisting of cerias, zirconas, perovskites, spinels, aluminas, titanias,  
25 and any mixtures thereof.

- Item 15. A ceramic layer according to any one of the preceding items, wherein said ceramic material is doped with a material selected from the group consisting of gadolinium and praseodymium for ceria, and yttria and scandia for zirconia,  
30 and any mixtures thereof.

- Item 16. A ceramic layer according to any one of the preceding items, wherein said binder is a polymeric binder.



Item 17. A ceramic layer according to any one of the preceding items, wherein said binder is selected from the group consisting of, poly(vinyl butyral) (PVB), cellulose ethers including methyl and ethyl cellulose, poly(vinyl alcohol) (PVA), poly(ethylene glycol) (PEG), poly(vinyl pyrrolidone) (PVP), poly(vinyl acetate),  
5 poly(vinyl methyl methacrylate) and any mixtures thereof.

Item 18. A ceramic layer according to item 17, wherein said binder is poly(vinyl butyral) (PVB).

10 Item 19. A ceramic layer according to any one of the preceding items, wherein said binder has a molecular weight between 10-200 kDa, such as 20-175 kDa, such as 30-150 kDa, such as 40-100 kDa, preferably 50-75 kDa.

Item 20. A ceramic layer according to any one of the preceding items, wherein  
15 said ceramic layer comprises at least one secondary plasticizer.

Item 21. A ceramic layer according to item 20, wherein said secondary plasticizer is poly (ethylene glycol) (PEG) or poly (propylene glycol) (PPG).

20 Item 22. A ceramic layer according to any one of the preceding items, wherein the average particle diameter (median) of the ceramic material in said ceramic layer is less than 1.0  $\mu\text{m}$ , such as less than 0.8  $\mu\text{m}$ , less than 0.6  $\mu\text{m}$ , less than 0.4  $\mu\text{m}$ , less than 0.3  $\mu\text{m}$ , preferably less than 0.2  $\mu\text{m}$ .

25 Item 23. A ceramic layer according to any one of the preceding items, wherein said ceramic layer comprises a releasing agent.

Item 24. A ceramic layer according to any one of the preceding items, wherein said ceramic layer comprises a de-foaming agent.

30

Item 25. A ceramic layer according to any one of the preceding items, wherein said ceramic layer comprises a flow modifier.

Item 26. A ceramic layer according to any one of the preceding items, wherein  
35 said ceramic layer comprises a wetting agent.

Item 27. A ceramic layer according to any one of the preceding items, wherein said ceramic layer is produced using a ceramic processing technique selected from the group consisting of, but not limited to, tape-casting, screen printing, extrusion, slip-casting, slot die coating and spraying, preferably tape casting.

5

Item 28. A ceramic layer according to any one of the preceding items, wherein said ceramic layer is a solid ceramic layer.

Item 29. A ceramic layer according to any one of the preceding items, wherein  
10 said ceramic layer is for use within solid oxide cell (SOC) technology.

Item 30. A ceramic layer according to any one of the preceding items, wherein said ceramic layer is for use within piezo-electronic technology.

15 Item 31. A solid oxide cell comprising a ceramic layer according to any of items 1-30.

Item 32. A piezo-electronic device comprising a ceramic layer according to any of items 1-30.

20

Item 33. A slurry for use in the manufacturing of a green ceramic layer comprising

- a ceramic material,
- a solvent
- a binder, and

25 - a dual-role dispersant and plasticizer,

wherein said dual role dispersant and plasticizer is an organic di- or tri-ester.

Item 34. A slurry according to item 33, wherein said solvent is an organic solvent.

30 Item 35. Use of an organic di- or tri-ester as a dispersant in the manufacturing of a slurry or green ceramic layer comprising a ceramic material.

Item 36. The use according to item 35, wherein said ceramic layer further comprises a binder.

35

Item 37. The use according to any one of items 35-36, wherein said ceramic layer is for use within solid oxide cell (SOC) technology.

Item 38. The use according to any one of items 35-36, wherein said ceramic layer  
5 is for use within piezoelectronic technology.

Item 39. A method of manufacturing a green ceramic layer comprising the steps of

- 10 a) mixing a dual role plasticizer and dispersant, a ceramic material and a solvent to provide a slurry
- b) milling the slurry provided in step a)
- c) adding a binder to the milled slurry provided in step b)
- d) optionally homogenizing said slurry of step c)
- e) optionally de-airing and filtering said slurry of step c) or d)
- 15 f) shaping said slurry provided in either of step c) to e) optionally using a support substrate to form a layer
- g) drying said slurry layer of step f) to provide said green ceramic layer, wherein said dual role dispersant and plasticizer is an organic di- or tri-ester.

20 Item 40. A method according to item 39 for the manufacture of a sintered ceramic layer, further comprising the step of

- h) optionally laminating said ceramic layer with further ceramic layers to form a multi-layered structure,
  - i) optionally performing a burnout of said ceramic layer
  - 25 j) sintering said ceramic layer(s),
- to provide a sintered ceramic layer.

Item 41. A method according to item 40, wherein said sintering is performed at a temperature of 600-1500 °C.

30

Item 42. A method according to any one of items 39-41, wherein said solvent is an organic solvent.

All patent and non-patent references cited in the present application, are hereby  
35 incorporated by reference in their entirety.

The invention will now be described in further details in the following non-limiting examples.

### Examples

5 Example 1 – Process for making a green ceramic layer with dual role dispersant and plasticizer

To provide a green ceramic layer according to the invention, a tape casting process was used as provided below. A custom build Pro-Cast series tape caster from HED International was used.

10

A thick dense layer of 8 mol% yttria stabilized zirconia (8YSZ) was prepared in order to demonstrate the effect in full scale for tributyl citrate.

First 12 g of tributyl citrate ( $\geq 97.0\%$ , Sigma-Aldrich) and 65 g of ethanol  
15 (anhydrous, 99.9 %, CCS Healthcare) were mixed in 1 L PE bottle. Then 150 g of 8YSZ and 1 kg. of 3/8 inch zirconia milling beads were added and the slurry was milled at approx. 200 rpm for 72 hours.

To prepare the binder mixture 49.2 g of PVB were added to 147.6 g of ethanol  
20 (anhydrous, 99.9 %, CCS Healthcare) in a 1 L PE bottle and mixed for 24 h at approx. 200 rpm. Then 18.5 g of PEG600 (average  $M_n$  600, waxy solid (moist), Sigma-Aldrich) and 30.8 g of tributyl citrate ( $\geq 97.0\%$ , Sigma-Aldrich) were added and mixed in over another 24 h at 200 rpm. The binder mixture was visually inspected after each step to ensure homogeneous mixing.

25

80.0 g of the binder mixture was then added to the milled slurry and the slurry was homogenized at 100 rpm for another 24 hours. The sample was then filtered using a 37 micron filter and additionally evacuated at 0.3 bar for 5 minutes.

30 The de-aired and filtered slurry was tape cast at both 100 and 1000 micron using a double blade setup and resulted in a tape free of cracks, agglomerates and other defects and with good strength and flexibility. The used blade gaps yields dried layer thicknesses of  $\approx 10\ \mu\text{m}$  and  $150\ \mu\text{m}$  respectively.

Circular samples were stamped out and sintered dense at temperatures in the range from 1250 – 1350 °C resulting in flat defect-free ceramics. The resulting microstructure can be seen in figure 7 (SEM picture of sintered sample). In figure 8 a picture of the green ceramic layer (tape) is displayed whereas figure 9 shows a picture of the sintered ceramic.

Example 2 – plasticization and other qualitative effects in selected binder systems comprising dual-role plasticizer and dispersant

Dried binder droplets were prepared by first dissolving the binder in the solvent over 24 hours and then mixing in the plasticizer/dispersant for an additional 24 hours. For this purpose 10 g of a polyvinyl butyral binder were added to 30 g of ethanol (anhydrous, 99.9 %, CCS Healthcare) in a 100 ml PE bottle and mixed for 24 h at approx. 200 rpm. A total of 10 g of plasticizers, with PEG600 being a secondary plasticizer, was then added in ratios as given in the table below and mixed in over another 24 h at 200 rpm. Samples were visually inspected after each step to ensure homogeneous mixing. Before evaluation, the mixtures were dried on a piece of plastic foil for at least 24 hours in order to ensure complete evaporation of the solvent. The samples were then visually inspected for chemical incompatibilities such as binder recrystallization (sample turns opaque (O)) or plasticizer migration (plasticizer appearing on surfaces as either droplets or a thin layer. This is also known as sweating (Sw)). The samples were then stretched by hand to give a qualitative estimate of strength (too strong (S) or too weak (W)) and flexibility (too flexible (F) or too inflexible (I)), meaning samples with no comments indicate good properties. Primary candidate indicates an optimal candidate and secondary candidate indicates a less good but acceptable candidate.

Entry	di- or tri ester	Amount (%w/w)	Binder	Amount (%w/w)	Sec. plasticizer	Amount (%w/w)	Comments
1	Triethyl citrate	50,0	PVB	50,0	PEG600	0,0	Good, secondary candidate
2		37,5		50,0		12,5	Very good, primary candidate

3		25,0		50,0		25,0	Opaque, strong and inflexible
4		12,5		50,0		37,5	Opaque, strong and inflexible
5		0,0		50,0		50,0	Opaque, strong and inflexible

Entry	di- or tri ester	Amount (%w/w)	Binder	Amount (%w/w)	Sec. plasticizer	Amount (%w/w)	Comments
1	Tributyl citrate	50,0	PVB	50,0	PEG600	0,0	Weak and flexible
2		37,5		50,0		12,5	Good, secondary candidate
3		25,0		50,0		25,0	Very good, primary candidate
4		12,5		50,0		37,5	Opaque, strong and inflexible
5		0,0		50,0		50,0	Opaque, strong and inflexible

Entry	di- or tri ester	Amount (%w/w)	Binder	Amount (%w/w)	Sec. plasticizer	Amount (%w/w)	Comments
1	Dibutyl maleate	50,0	PVB	50,0	PEG600	0,0	Weak and flexible

Entry	di- or tri ester	Amount (%w/w)	Binder	Amount (%w/w)	Sec. plasticizer	Amount (%w/w)	Comments
2		37,5		50,0		12,5	Weak and flexible
3		25,0		50,0		25,0	Very good, primary candidate
4		12,5		50,0		37,5	Opaque, strong and inflexible
5		0,0		50,0		50,0	Opaque, strong and inflexible
6		20,0		60,0		20,0	Good, secondary candidate
7		15,0		70,0		15,0	Strong and inflexible

Entry	di- or tri ester	Amount (%w/w)	Binder	Amount (%w/w)	Sec. plasticizer	Amount (%w/w)	Comments
1	Triethyl 2-acetylcitrate	50,0	PVB	50,0	PEG600	0,0	Opaque and sweating
2		37,5		50,0		12,5	Very good, primary candidate
3		25,0		50,0		25,0	Opaque, sweating, strong and inflexible

4		12,5		50,0		37,5	Opaque, sweating, strong and inflexible
5		0,0		50,0		50,0	Opaque, strong and inflexible

Entry	di- or tri ester	Amount (%w/w)	Binder	Amount (%w/w)	Sec. plasticizer	Amount (%w/w)	Comments
1	Tributyl 2-acetylcitrate	50,0	PVB	50,0	PEG600	0,0	Opaque, sweating, weak, flexible
2		37,5		50,0		12,5	Good, secondary candidate
3		25,0		50,0		25,0	Very good, primary candidate
4		12,5		50,0		37,5	Strong and inflexible
5		0,0		50,0		50,0	Opaque, strong and inflexible

The properties of the binder systems are also disclosed graphically in figures 1-5. For all five plasticizer/dispersants good candidates were available at specific

5 concentration of the three listed components. The results of these more qualitative tests have also been directly transferable to real tapes including ceramics and the dual role component acting efficiently in both roles.



Example 3 – Dispersion effects demonstrated in the slurry state for selected ceramic layers

The dispersion abilities of the compounds of the invention were tested.

Samples were prepared by adding 4 g of the dispersant, 100 g of 3 mol% yttria  
 5 stabilized zirconia (3YSZ) and 250 g of ethanol (anhydrous, 99.9 %, CCS  
 Healthcare) to a 1 L PE bottle and milling for 48 h with 1 kg of 3/8 inch zirconia  
 milling beads.

Sedimentation speed and final packing were then measured using a Formulation  
 Turbiscan Lab model and particle sizes were measured using a Beckman Coulter  
 10 LS 13320.

Dispersant	Sedimentation velocity (mm/h)	Packing (%)	D10 ( $\mu\text{m}$ )	D25 ( $\mu\text{m}$ )	D50/Median ( $\mu\text{m}$ )	D75 ( $\mu\text{m}$ )	D90 ( $\mu\text{m}$ )
None (reference)	0,94	39	0,127	0,337	1,025	1472	1,823
2.5 dwb% PVP (Reference)	0,05	77	0,082	0,113	0,197	0,848	1,487
4 dwb% Diethyl tartrate	0,05	75	0,080	0,106	0,175	0,875	1,570
4 dwb% Triethyl citrate	0,12	65	0,084	0,113	0,181	0,770	1,335
8 dwb% Triethyl citrate	0,10	69	0,083	0,111	0,181	0,798	1,402
4 dwb% Tributyl citrate	0,12	60	0,084	0,115	0,192	0,817	1,397

Dispersant	Sedimentation velocity (mm/h)	Packing (%)	D10 (µm)	D25 (µm)	D50/Median (µm)	D75 (µm)	D90 (µm)
4 dwb% Glyceryl triacetate	0,15	72	0,084	0,126	0,242	1,004	1,514
4 dwb% Dibutyl maleate	0,56	52	0,087	0,161	0,399	1,117	1,541
4 dwb% Glyceryl tributyrat	0,69	52	0,115	0,226	0,797	1,185	1,570
4 dwb% Triethyl 2-acetylcitrate	0,83	44	0,103	0,236	0,818	1,148	1,378
4 dwb% Tributyl 2-acetylcitrate	0,84	46	0,138	0,303	0,907	1,264	1,623
4 dwb% Glyceryl trioctanoate	0,92	46	0,115	0,232	0,706	1,122	1,440

For a good dispersant the sedimentation speed should be as slow as possible.

According to Stokes' Law, the speed decreases with decreasing particle size.

Samples which are not re-agglomerating or flocculating will in general pack better  
 5 and the packing should thus be as high as possible. The D10 to D90 are direct measurements of fractions below a certain particle size and should be as low as possible for a good dispersant.

From the above examples diethyl tartrate, triethyl citrate, tributyl citrate and  
 10 glyceryl triacetate shows excellent dispersing properties similar to a state of the art dispersant such as PVP.

Dibutyl maleate and glyceryl tributyrat also have strong dispersing properties.

Triethyl 2-acetylcitrate, tributyl 2-acetylcitrate and glyceryl trioctanoate still show some dispersing properties in the form of slower sedimentation rates, better packing and/or smaller particle sizes.

- 5 In conclusion the combined dispersant and plasticizers of the present invention have excellent dispersant properties as compared to using no dispersant, and they have equal or comparable dispersant properties as compared to prior art dispersants, which do not have plasticizing effects (see also figure 6).

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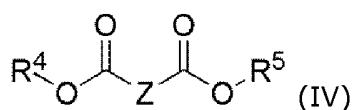
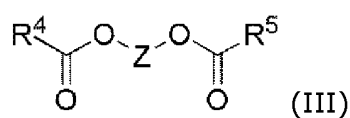
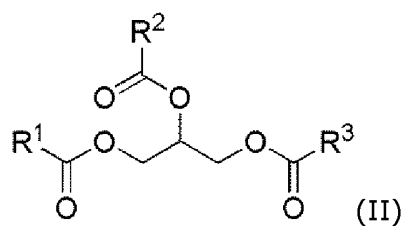
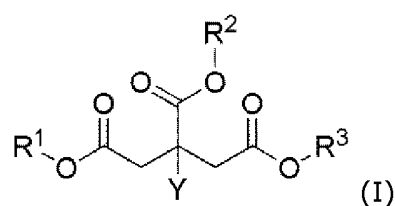
**Claims**

1. A green ceramic layer comprising

- a ceramic material,
- a binder, and

5       - a dual-role dispersant and plasticizer,

wherein said dual-role dispersant and plasticizer is an organic di- or tri-ester selected from a compound of formula (I), (II), (III) or (IV)



wherein

20       R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are independently selected from C<sub>1</sub>-C<sub>9</sub> alkyl and hydrogen, with the proviso that at least two of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> is a C<sub>1</sub>-C<sub>9</sub> alkyl,

Y is hydrogen or hydroxyl,

R<sup>4</sup> and R<sup>5</sup> are independently selected from C<sub>1</sub>-C<sub>9</sub> alkyl,

Z is C<sub>1</sub>-C<sub>6</sub> alkylene or C<sub>2</sub>-C<sub>6</sub> alkenylene wherein said alkylene or alkenylene is optionally substituted with hydroxyl.

2. A ceramic layer according to claim 1, wherein said ceramic layer comprises no further dispersants.
3. A ceramic layer according to any of the preceding claims, wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are independently selected from  $C_1$ - $C_6$  alkyl and hydrogen, with the proviso that at least two of  $R^1$ ,  $R^2$  and  $R^3$  is a  $C_1$ - $C_6$  alkyl.
4. A ceramic layer according to any of the preceding claims, wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are independently selected from  $C_1$ - $C_6$  alkyl
- 10 Y is hydroxyl  
Z is  $C_1$ - $C_6$  alkylene wherein said alkylene is optionally substituted with hydroxyl.
5. A ceramic layer according to any of the preceding claims, wherein Z is –  $(CH_2)_m(CH[OH])_p(CH_2)_n$ –, and wherein m, p and n independently are an integer  
15 between 0 and 6, with the proviso that  $m+p+n$  is an integer between 1 and 6.
6. A ceramic layer according to any of the preceding claims, wherein Z is selected from the group consisting of  $-CH_2CH[OH]CH_2-$ ,  $CH_2CH[OH]-$ , and  $-CH[OH]CH[OH]-$ .
- 20
7. A ceramic layer according to any one of the preceding claims, wherein said organic di- or tri-ester is a di- or tri-ester of a carboxylic acid or a polyol selected from the group consisting of citric acid, oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid, glutaric acid, adipic acid, malic acid, tartaric acid,  
25 ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexamethylene glycol and glycerol.
8. A ceramic layer according to claim 7, wherein said organic di- or tri-ester is a di- or tri-ester of a carboxylic acid or a polyol selected from the group consisting  
30 of citric acid, malic acid, tartaric acid and glycerol.
9. A ceramic layer according to any one of the preceding claims, wherein said organic di- or tri-ester is selected from the group consisting of triethyl citrate, tributyl citrate, glyceryl triacetate and diethyl tartrate.

10. A ceramic layer according to any one of the preceding claims, wherein said organic di- or tri-ester comprises no alkyl chains comprising more than 9 carbons, such as preferably 8 carbons, 7 carbons, 6 carbons, 5 carbons, most preferably 4 carbons.

5

11. A ceramic layer according to any one of the preceding claims, wherein said dual role dispersant and plasticizer is present in amount of 0.1-30%(dwb), 0.2-25%(dwb), 0.5-20%(dwb), 1-18%(dwb), 2-17%(dwb), 3-16%(dwb), 5-15%(dwb), 8-12%(dwb), 9-11%(dwb), such as around 10%(dwb).

10

12. A ceramic layer according to any one of the preceding claims, wherein said ceramic material is a powder.

13. A ceramic layer according to any one of the preceding claims, wherein said  
15 ceramic material is a metal oxide or mixed oxide, preferably selected from the group consisting of cerias, zirconas, perovskites, spinels, aluminas, titanias, and any mixtures thereof.

14. A ceramic layer according to any one of the preceding claims, wherein said  
20 ceramic material is doped with a material selected from the group consisting of gadolinium and praseodymium for ceria, and yttria and scandia for zirconia, and any mixtures thereof.

15. A ceramic layer according to any one of the preceding claims, wherein said  
25 binder is a polymeric binder.

16. A ceramic layer according to any one of the preceding claims, wherein said binder is selected from the group consisting of, poly(vinyl butyral) (PVB), cellulose ethers including methyl and ethyl cellulose, poly(vinyl alcohol) (PVA),  
30 poly(ethylene glycol) (PEG), poly(vinyl pyrrolidone) (PVP), poly(vinyl acetate), poly(vinyl methyl methacrylate) and any mixtures thereof.

17. A ceramic layer according to claim 16, wherein said binder is poly(vinyl butyral) (PVB).

35

18. A ceramic layer according to any one of the preceding claims, wherein said binder has a molecular weight between 10-200 kDa, such as 20-175 kDa, such as 30-150 kDa, such as 40-100 kDa, preferably 50-75 kDa.
- 5 19. A ceramic layer according to any one of the preceding claims, wherein said ceramic layer comprises at least one secondary plasticizer.
20. A ceramic layer according to claim 19, wherein said secondary plasticizer is poly (ethylene glycol) (PEG) or poly (propylene glycol) (PPG).
- 10 21. A ceramic layer according to any one of the preceding claims, wherein the average particle diameter (median) of the ceramic material in said ceramic layer is less than 1.0  $\mu\text{m}$ , such as less than 0.8  $\mu\text{m}$ , less than 0.6  $\mu\text{m}$ , less than 0.4  $\mu\text{m}$ , less than 0.3  $\mu\text{m}$ , preferably less than 0.2  $\mu\text{m}$ .
- 15 22. A ceramic layer according to any of the preceding claims, wherein the thickness of the ceramic layer ranges from 100 nm to 10 cm, such as 0.5  $\mu\text{m}$  to 1 cm, preferably 1  $\mu\text{m}$  – 1 mm.
- 20 23. A ceramic layer according to any one of the preceding claims, wherein said ceramic layer comprises a releasing agent.
24. A ceramic layer according to any one of the preceding claims, wherein said ceramic layer comprises a de-foaming agent.
- 25 25. A ceramic layer according to any one of the preceding claims, wherein said ceramic layer comprises a flow modifier.
26. A ceramic layer according to any one of the preceding claims, wherein said
- 30 ceramic layer comprises a wetting agent.
27. A ceramic layer according to any one of the preceding claims, wherein said ceramic layer is produced using a ceramic processing technique selected from the group consisting of, but not limited to, tape-casting, screen printing, extrusion,
- 35 slip-casting, slot die coating and spraying, preferably tape casting.

28. A ceramic layer according to any one of the preceding claims, wherein said ceramic layer is a solid ceramic layer.
29. A ceramic layer according to any one of the preceding claims, wherein said  
5 ceramic layer is for use within solid oxide cell (SOC) technology.
30. A ceramic layer according to any one of the preceding claims, wherein said ceramic layer is for use within piezo-electronic technology.
- 10 31. A solid oxide cell comprising a ceramic layer according to any of claims 1-30.
32. A piezo-electronic device comprising a ceramic layer according to any of claims 1-30.
- 15 33. A slurry for use in the manufacturing of a green ceramic layer comprising
- a ceramic material,
  - a solvent
  - a binder, and
  - a dual-role dispersant and plasticizer,
- 20 wherein said dual role dispersant and plasticizer is an organic di- or tri-ester.
34. A slurry according to claim 33, wherein said solvent is an organic solvent.
35. A slurry according to any one of claims 33-34, wherein the slurry containing  
25 the ceramic materials has a viscosity ranging from 1 mPa · s to 100 Pa · s,  
preferably from 10 mPa · s to 10 Pa · s.
36. Use of an organic di- or tri-ester as a dispersant in the manufacturing of a slurry or green ceramic layer comprising a ceramic material.
- 30 37. The use according to claim 36, wherein said ceramic layer further comprises a binder.
38. The use according to any one of claims 36-37, wherein said ceramic layer is  
35 for use within solid oxide cell (SOC) technology.



39. The use according to any one of claims 36-37, wherein said ceramic layer is for use within piezoelectronic technology.

40. A method of manufacturing a green ceramic layer comprising the steps of

- 5           a) mixing a dual role plasticizer and dispersant, a ceramic material and a solvent to provide a slurry  
            b) milling the slurry provided in step a)  
            c) adding a binder to the milled slurry provided in step b)  
            d) optionally homogenizing said slurry of step c)  
10          e) optionally de-airing and filtering said slurry of step c) or d)  
            f) shaping said slurry provided in either of step c) to e) optionally using a support substrate to form a layer  
            g) drying said slurry layer of step f) to provide said green ceramic layer, wherein said dual role dispersant and plasticizer is an organic di- or tri-ester.

15

41. A method according to claim 40, wherein said manufacturing of a green ceramic layer is performed at a temperature of 0-50 °C, preferably at 5-40 °C, more preferably at 10-35 °C, even more preferably at 15-30 °C.

20 42. A method according to any one of claims 40-41 for the manufacture of a sintered ceramic layer, further comprising the step of

- h) optionally laminating said ceramic layer with further ceramic layers to form a multi-layered structure,  
            i) optionally performing a burnout of said ceramic layer  
25          j) sintering said ceramic layer(s),  
to provide a sintered ceramic layer.

43. A method according to claim 42, wherein said sintering is performed at a temperature of 600-1500 °C.

30

44. A method according to any one of claims 40-43, wherein said solvent is an organic solvent.

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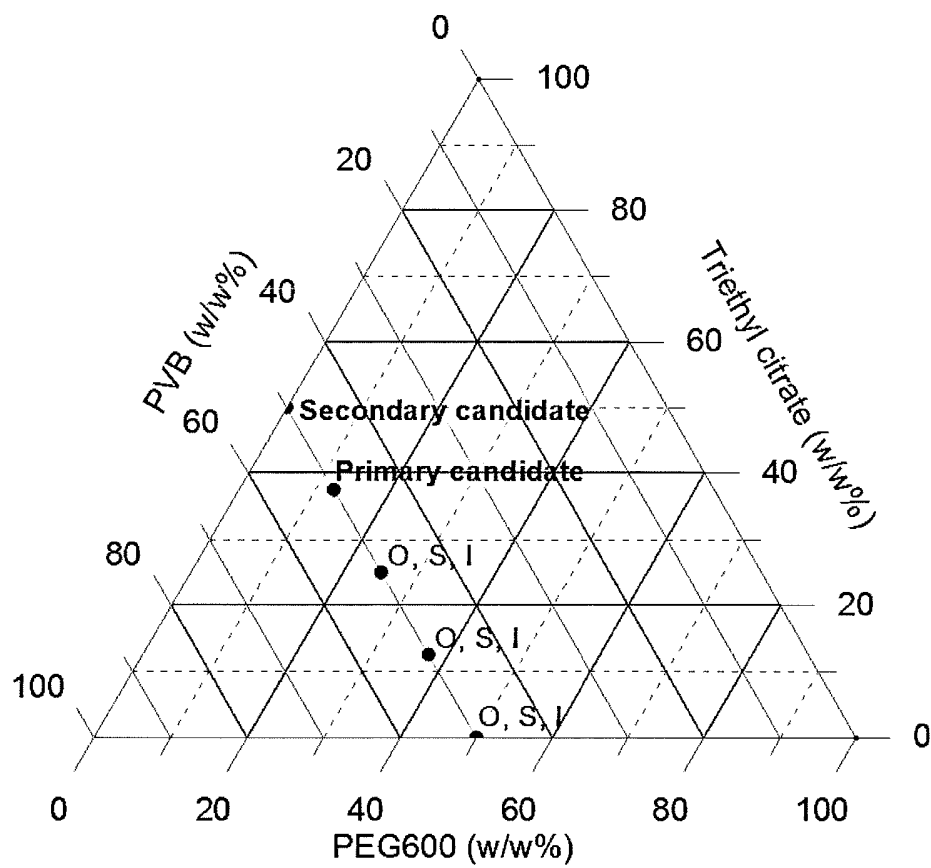


Fig. 1

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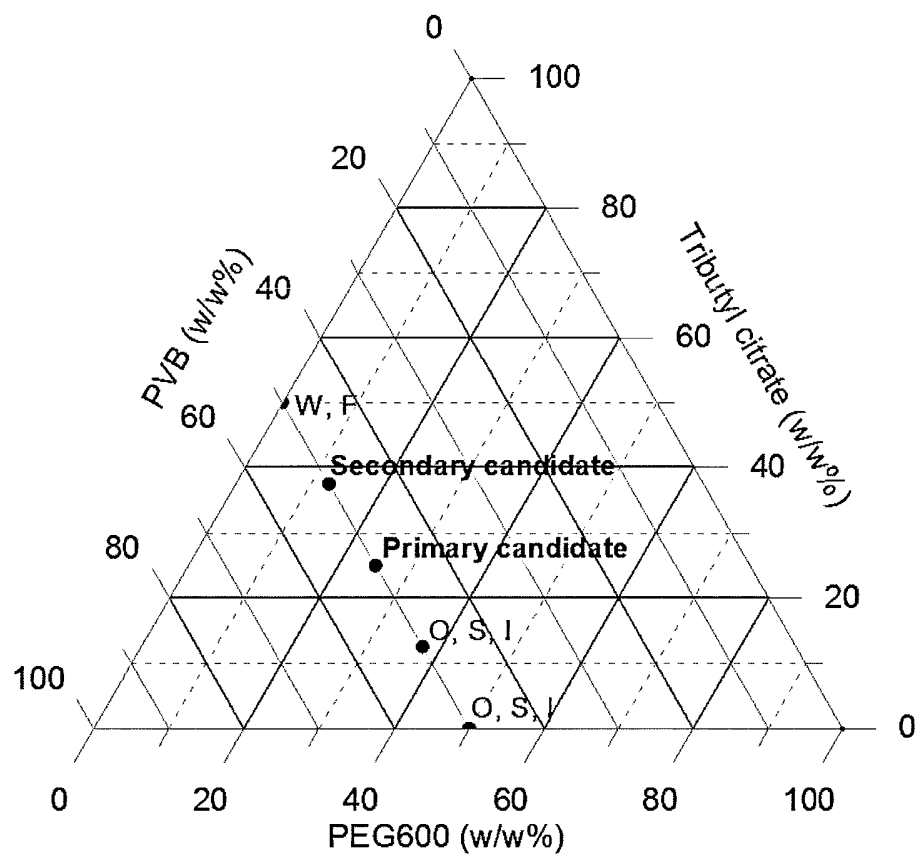


Fig. 2

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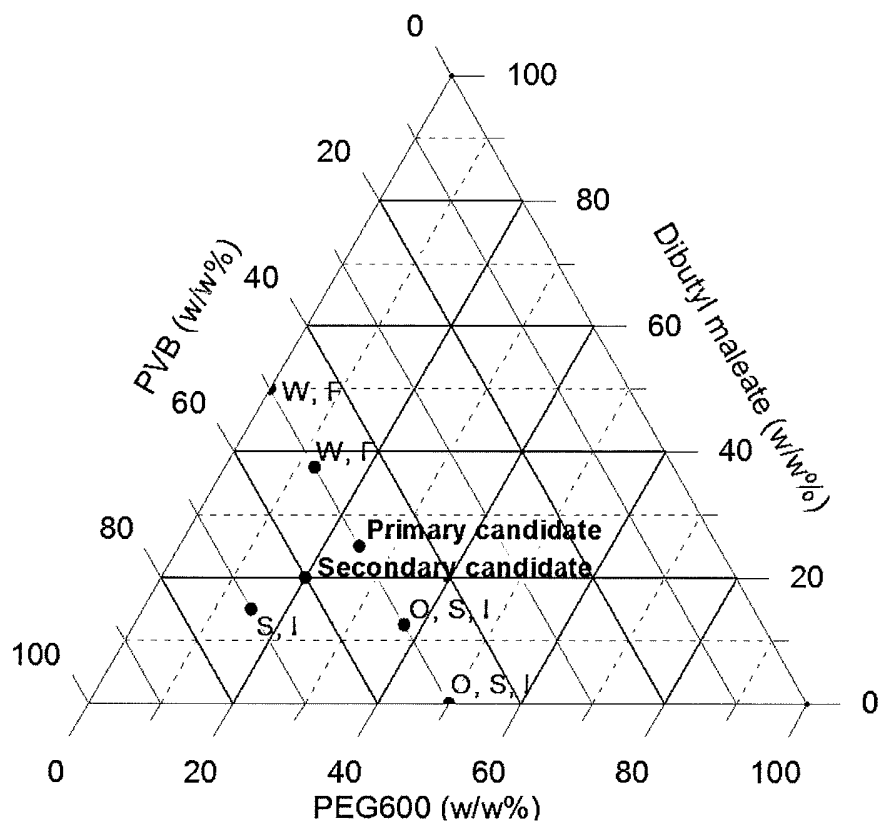


Fig. 3

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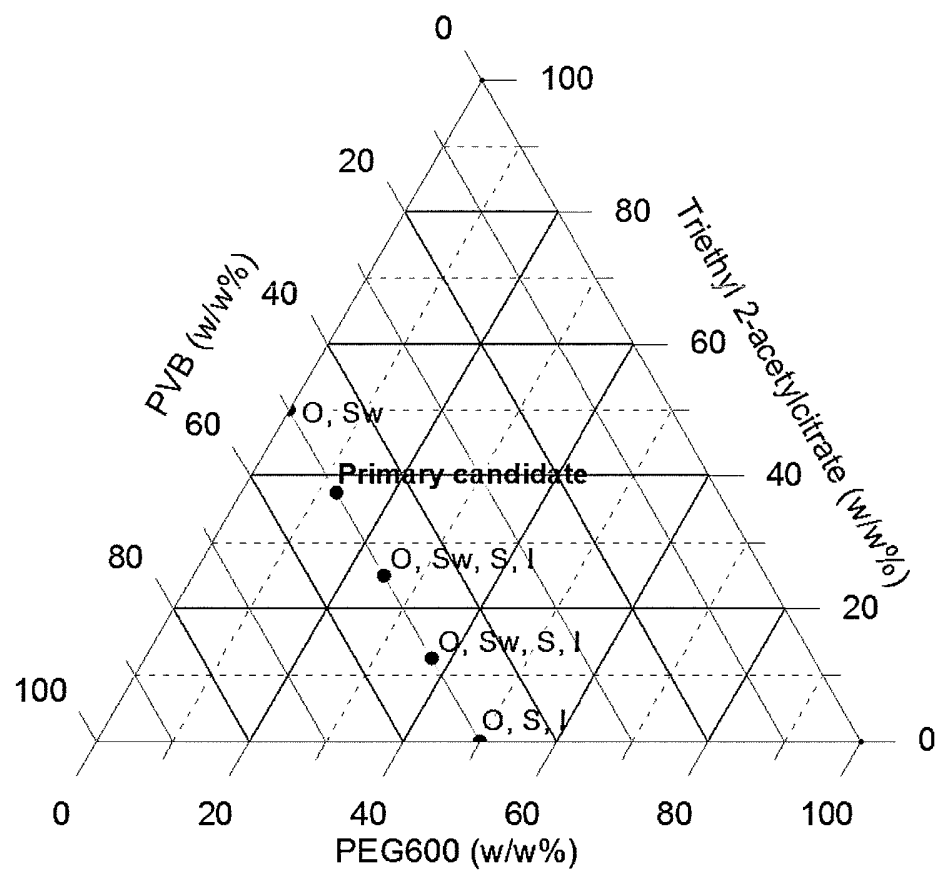


Fig. 4

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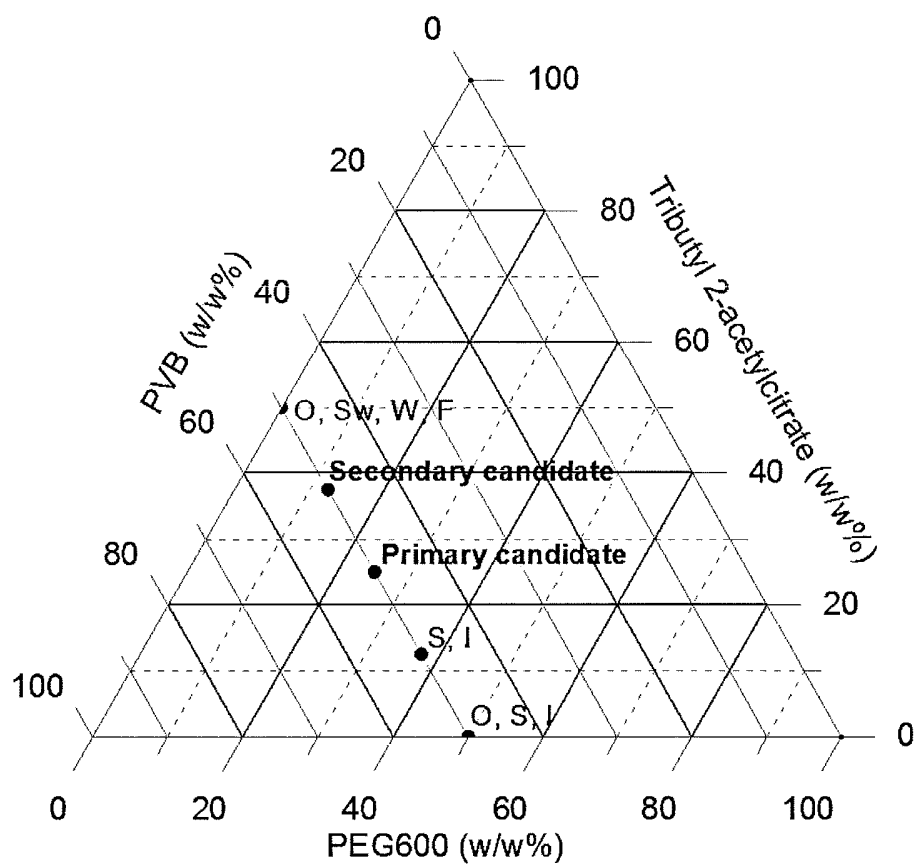


Fig. 5

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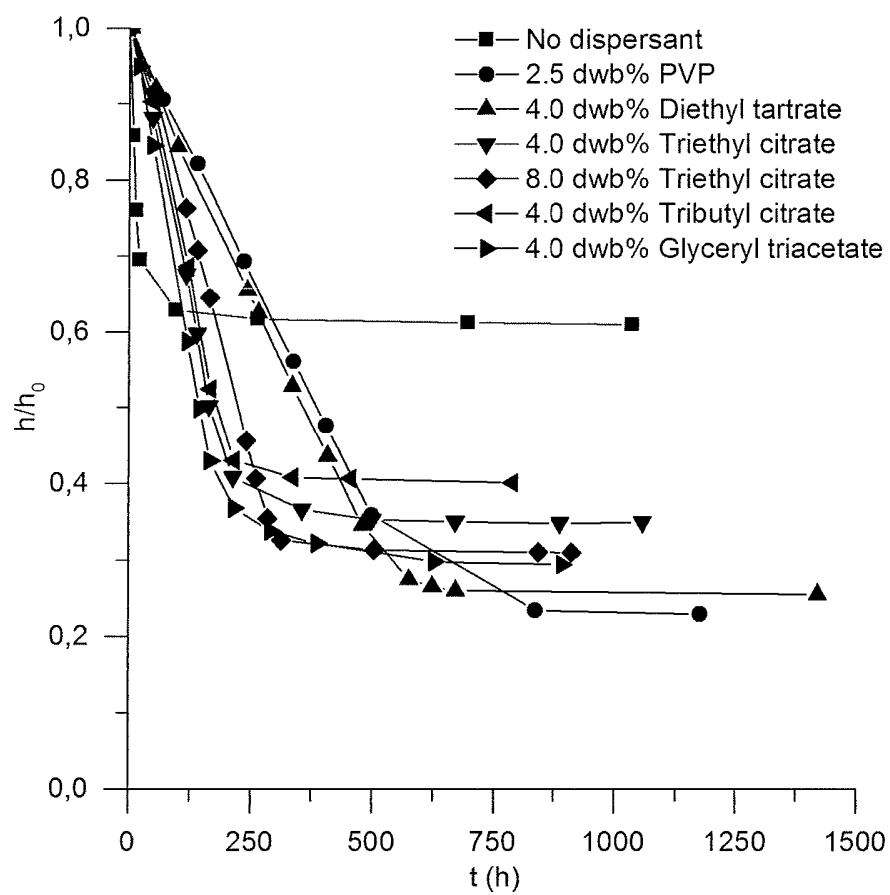


Fig. 6

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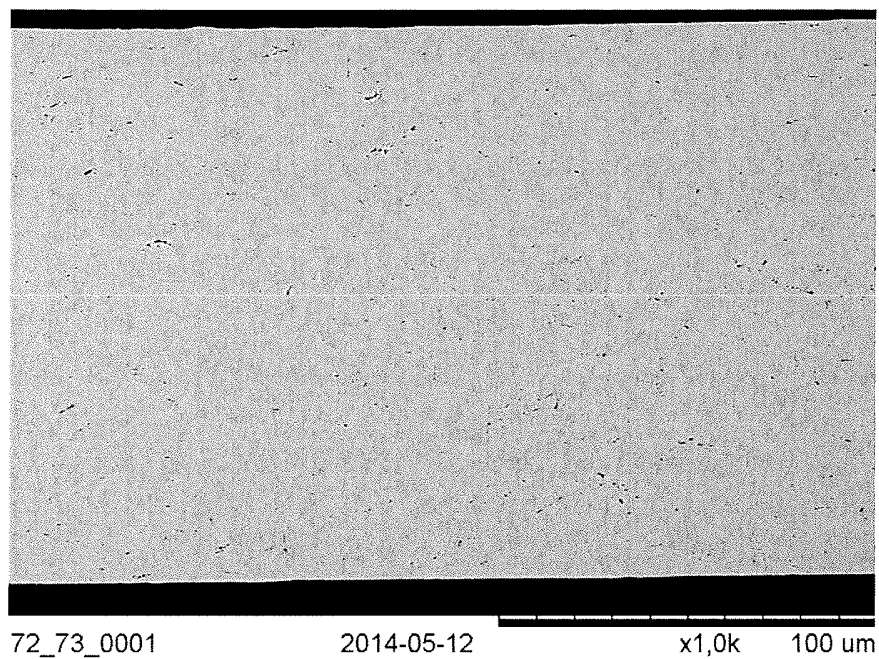


Fig. 7

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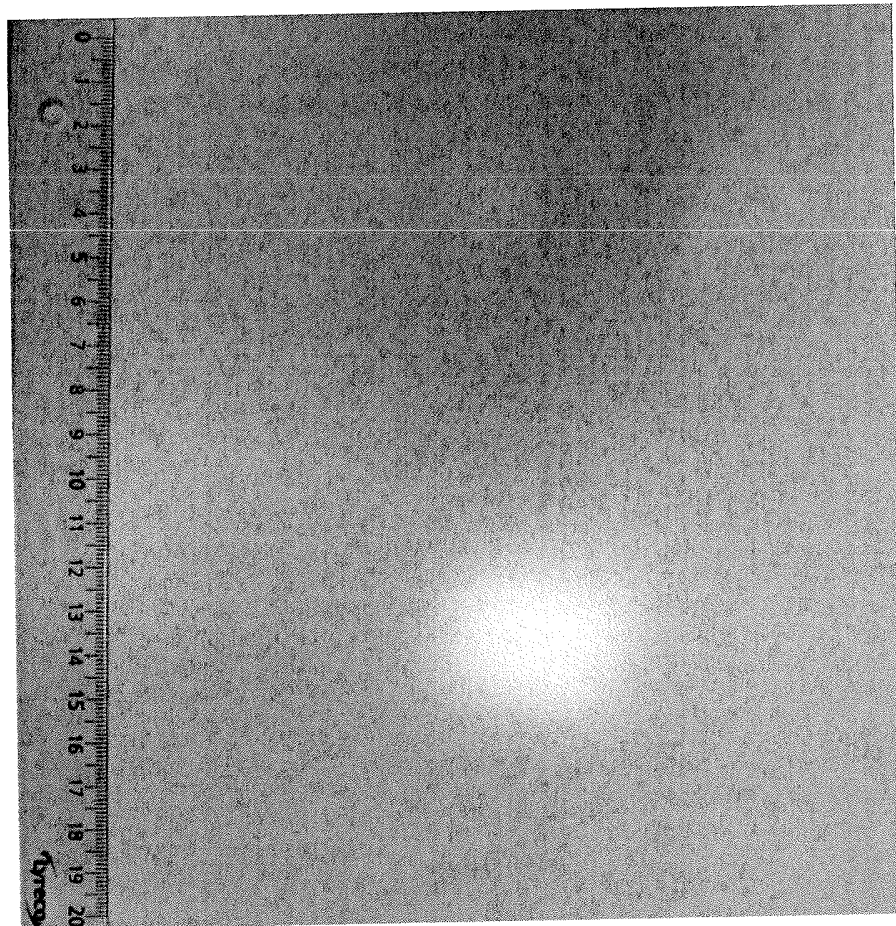


Fig. 8

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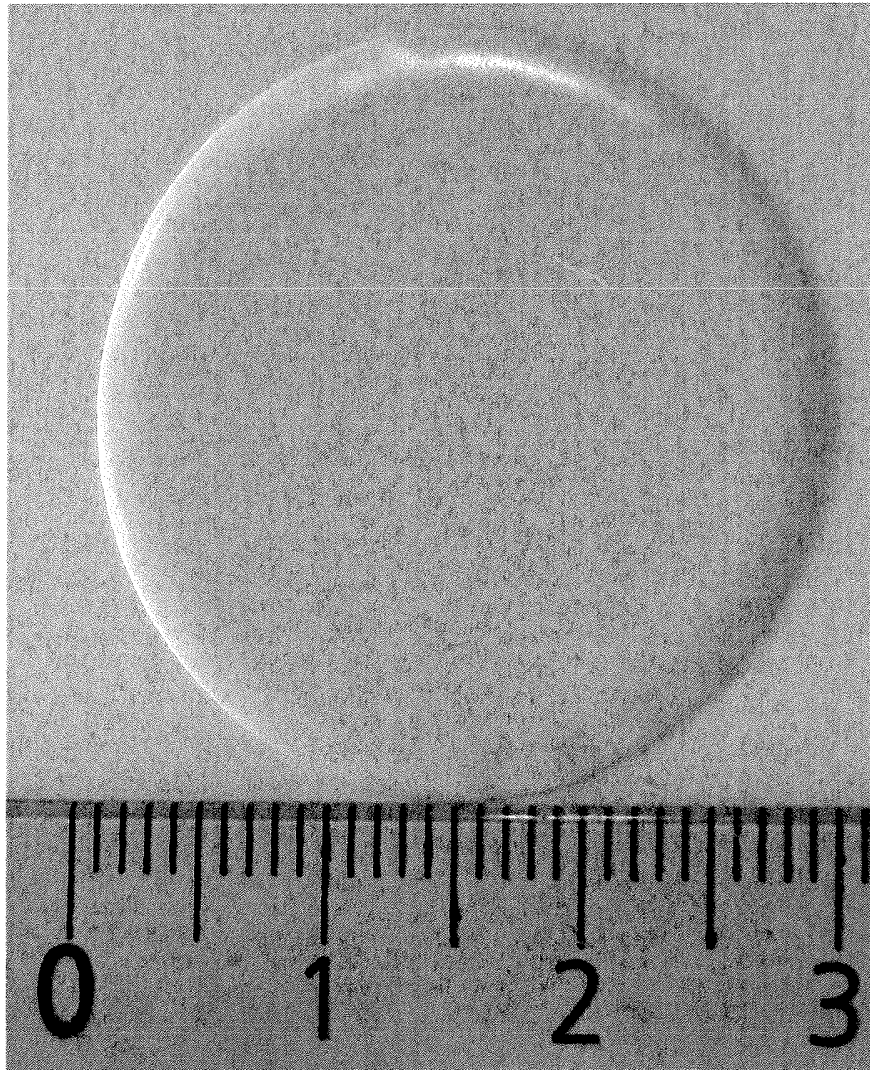


Fig. 9

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# INTERNATIONAL SEARCH REPORT

International application No

PCT/DK2015/050330

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C04B35/622 B32B18/00 C04B35/632 C08K5/00 C08K5/10 C08K5/11 C04B35/111 C04B35/443 C04B35/46 C04B35/486 C04B35/50 C04B35/626 C04B35/634		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) C04B B32B C08K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 552 913 A1 (NGK INSULATORS LTD [JP]) 13 July 2005 (2005-07-13) paragraphs [0008], [0030] - [0036], [0050], [0051], [0061] - [0067]; figures 1,2 -----	1-44
X	EP 1 832 337 A1 (KARLSRUHE FORSCHZENT [DE]) 12 September 2007 (2007-09-12) paragraphs [0009], [0015] - [0019]; table 1 -----	1-32, 36-39
A	JP H01 261251 A (KORANSHA KK) 18 October 1989 (1989-10-18) the whole document -----	1-44
A	DE 42 33 340 A1 (BASF AG) 7 April 1994 (1994-04-07) the whole document -----	1-44
<div style="display: flex; justify-content: space-between;"> <span><input type="checkbox"/> Further documents are listed in the continuation of Box C.</span> <span><input checked="" type="checkbox"/> See patent family annex.</span> </div>		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">2 March 2016</div>		Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">11/03/2016</div>
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-size: 1.2em;">Bonneau, Sébastien</div>

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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